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<b>(54) Title:</b> MULTI-LAYER HIGH OPACITY FILM STRUCTURES		
<b>(57) Abstract</b>		
<p>An opaque, biaxially oriented polymeric film structure, of: a thermoplastic polymer matrix core layer having a first surface and a second surface, within said core is located a plurality of voids having positioned in at least a substantial number of said voids is at least one spherical void-initiating particle which is phase distinct and incompatible with the matrix material, the void space occupied by the particle being substantially less than the volum of the void, with one generally cross-sectional dimension of the particle at least approximately corresponding to the cross-sectional dimension of the void; the population of the voids in the core being such as to cause a significant degree of opacity; and an ink receptive skin layer made up of an ethylene polymer having a density of 0.926 to 0.965 adhering to the first surface of the core layer. In the embodiment of this invention where this composite film is used as label stock, there is also provided an adhesive on an exposed surface of the second thermoplastic skin layer.</p>		

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MULTI-LAYER HIGH OPACITY FILM STRUCTURES  
OF IMPROVED WHITENESS AND MACHINABILITY

5        This invention relates to polymer films of enhanced opacity and to a method of making such films. It more particularly refers to a biaxially oriented composite film structure having improved properties, including glossiness, ink adhesion and printed ink retention.

10       In the packaging of certain types of foods, such as snack foods like potato chips and cookies, it is common practice to employ a multi-layer film. A desirable property in such a packaging film is its opacity which serves to protect the packaging and the product contained therein from deterioration  
15       caused by exposure to light. In particular, it has been found that when the package is exposed to certain wavelengths of light, specifically up to about 450 nm, increased spoilage in some packaged products results. Thus, the degree of opacity which is present in the film has been found to be a significant  
20       parameter, because it has been found that spoilage of the contents of the package occurs even if the film allows the passage of only some light.

      Despite advances in the art, a need still exists for a film structure of high opacity which has improved processing  
25       characteristics, machinability and printability, while also providing high whiteness, strength and stiffness.

      Accordingly, it is an object of the present invention to provide a film structure of high opacity.

      It is another object of the present invention to provide  
30       a film structure with improved machinability.

      It is a further object of the present invention to provide a film structure having an improved range of process operability.

      It is yet another object of the present invention to  
35       provide a film which may be bonded to a wide variety of substrates and coatings.

      It is a yet further object of the present invention to

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provide a multi-layer film structure of high whiteness.

It is a still further object of this invention to provide a composite film structure having at least one surface which has a significantly improved adhesion to inks.

- 5 It is a still further object of this invention to provide a composite film structure having at least one surface which has a significantly improved adhesion to U V cured inks.

In accord with and fulfilling these objects, the film structure of the present invention is an opaque, biaxially  
10 oriented, multilayer polymeric film. The film structure includes:

(a) a biaxially orientable thermoplastic polymer core layer having a first surface and a second surface; and

- (b) a first thermoplastic polymer skin layer having a first  
15 surface and a second surface, wherein the first surface of the first skin layer is adhered to the first surface of the core layer. The second surface of this first thermoplastic polymer skin should be composed of a polymeric material which has excellent ink adhesion. According to this invention, it is  
20 preferred that at least this second surface is medium density polyethylene; and wherein the skin layer(s) are of a thickness such that the outer surface of the skin layers do not, at least substantially, manifest any of the surface irregularities which may be present in said matrix core layer. The skin layer(s) (b)  
25 can be simple, economic, thin encapsulating layers, or they can be more elaborate, heat sealable layers.

According to one aspect of this invention, the core layer and the skin layer may both be substantially transparent. In this embodiment of this invention, both the core layer and the  
30 skin layer should be substantially transparent, that is neither should have opacity inducing agents, or cavitation therein.

According to another aspect of this invention, the core layer may be opaque. In this embodiment of this invention, the core layer may be made up of a matrix of a polymer film  
35 containing a multiplicity of voids. Positioned within at least a substantial number of these voids are at least one void-initiating particle, which is in a phase which is distinct from

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and incompatible with the matrix material, and is preferably a substantially spherical particle. The void space occupied by the particle is substantially less than the volume of the void, and the population of the voids in the core is such as to cause  
5 a significant degree of opacity.

In a further embodiment of this invention, the core material, whether it is opaque or transparent, may have a second under-skin, referred to as layer (c), disposed thereon, on the opposite side thereof to the ink receptive skin layer (b)  
10 referred to above. This second thermoplastic polymer skin layer has a first surface and a second surface, wherein the first surface of the second skin layer is adhered to the second surface of the core layer. The second skin layer may also contain, substantially uniformly dispersed therethrough,  
15 inorganic material in an amount effective to impart desired characteristics to the surface of the composite film, such as opacity or antiblocking characteristics, and means to decrease the inherent film-to-film coefficient of friction at the second, exposed surface of the second thermoplastic polymer skin layer.  
20 It is also possible to tailor the properties and characteristics of this second under-skin (c) to its desired end use. Thus, in addition to, or instead of, its having anti-blocking characteristics, it may be more readily heat sealable. Other characteristics may be imparted, as desired without adversely  
25 affecting the characteristics and the properties of the core layer or the ink receptive layer of the film of this invention.

It has been found that, in addition to its desirable opaque character, a cavitated layer also has the unexpected property of being more easily and readily die-cut, than a non-cavitated  
30 layer of the same composition and structure. Thus, in making a label stock, if the label is made of a composite multilayered film form material, comprising a cavitated core layer and a cavitated skin layer on the side thereof opposite to the side having improved ink receptivity according to this invention, the  
35 label also has improved die cuttability, which is a significant advantage over label stock which has conventional die cuttability. In this construction, the die cutting will proceed

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with the die penetrating the print skin (b), then the core layer (a), then the under skin (c), with the core (a) and the underskin (c) both being cavitated.

The skin layer(s) may contain up to about 12% by weight of titanium dioxide contact pigment. This is desirable, but not necessary, in order to increase the apparent whiteness of the composite film product.

This invention also provides a process for preparing an improved biaxially oriented polymeric film structure, comprising the steps of:

- (a) forming a composition comprising a first thermoplastic polymeric material which is suitable for use as a core layer;
- (b) heating the core layer mixture produced in step (a) to a temperature which is at least above the melting point, or the glass transition temperature, of the first thermoplastic polymeric material;
- (c) providing a medium or high density polyethylene, second thermoplastic polymeric material, if desired mixed with titanium dioxide contact pigment;
- (d) coextruding said first and second thermoplastic polymers to produce a composite film structure comprising the core layer, and the medium to high density polyethylene containing first skin layer; and
- (e) biaxially orienting said composite film structure.

According to one aspect of the process embodiment of this invention, where it is desired to make an opaque composite film, the core portion of the film can be made by admixing the first thermoplastic polymeric material with a minor proportion of a first material, which is incompatible with the first polymeric material, and which has a higher melting point, or a higher glass transition temperature, than the first polymeric material, to produce a core layer mixture. The skin layer (b) can have the same composition as set forth above, and these can be coextruded in the conventional manner to form a suitable composite film. Biaxial orientation of this composite film will cause it to become opaque.

A further aspect of this invention includes the use of the

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composite film of this invention as ink indicia receiving means. That is, the composite film of this invention is not only sufficiently opaque to substantially prevent incident light from penetrating and spoiling the contents of a package made from this film, or in the alternative is sufficiently transparent to allow it to be seen through, as desired, but it also has a unique surface which has substantially improved ink receptivity. According to this aspect of this invention, the particular polymer which constitutes the film on the ink receiving side of the composite film structure of this invention must be designated with particularity.

From an opacity perspective, the composition of the skin layer(s) are not so important as the composition of the core layer and the relative thickness of the core and skin layers. In order for the product to be transparent, the composition of all of the layers must be carefully considered and controlled. From an ink receptivity perspective, the composition of the skin layer (b) has been found to be an essential feature of this aspect of this invention. Thus, according to this aspect of this invention, the ink receiving side of the composite film structure is preferably a medium to high density ethylene polymer having a density in the range of about 0.926 to 0.965 g/cc, or an ethylene-propylene-butene terpolymer. There ink receptive surfaces, or skin compositions, have been found to have substantially improved ink receptivity as compared to the more conventional surface of this type of polymer film, polypropylene. Where the ink is of the U V cured type, it is much preferred to use a medium density ethylene homopolymer as the composition of the skin layer (b). In this use, high density polyethylene is better than polypropylene in terms of ink receptivity and adherence. However, in the specific instance where the ink is cured through the use of ultraviolet light, it has been found that the subset of medium density polyethylene is better than high density polyethylene in terms of ink receptivity and adhesion.

In order to achieve the unique opaque film composite structure of the present invention, it is important that a

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particular relationship exist between the thickness dimension of the core and the thickness dimension of the skin layers. It is preferred that the core thickness be from about 60 to about 95% of the thickness of the overall structure, with a core thickness of at least about 65% of the total thickness being especially preferred. It is preferred that the total thickness of the film structure be at least about 1 mil. Thicker or thinner composite films, for example of about 0.5 mil or greater, are suitable where the composite film is transparent.

These features, that is the relative thickness of the core layer as well as the minimum overall thickness of the composite film, in combination with defining the population and configuration of the voids in the core portion of the composite film determine and materially contribute to the overall degree of opacity of the composite film structure of this invention. By maintaining the thickness of the skin layers within particular ranges in relation to the thickness of the overall structure and in relation to the thickness of the core layer, the overall combination results in unique advantages.

In the embodiment of this invention where the composite film is opaque, the first skin layer (b), which is adhered to the first surface of the core layer (a), and the second skin layer (c), which is adhered to the second surface of core layer (a), each suitably have a thickness of from about 5 to about 30% of the thickness of the overall structure. The thickness of these skin layers is preferably about 5 to about 15 % of the total thickness of the composite film. In the embodiment of this invention where the composite film is substantially transparent, the skin film(s) should be substantially thinner. In this embodiment, the skin layer should be up to about 1% of the thickness of the composite film.

In addition to serving as the ink receptive portion and the sliding surface of the composite film of this invention, these skin layers also serve an important function in assisting to control the rate of water vapor transmission (WVTR) through the composite film having a cavitated core structure. The core is a thermoplastic polymer matrix material within which is located



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a multiplicity of voids. From this description, it is to be understood that the core matrix configuration is a combination of the thermoplastic polymer core material and the voids therein.

- 5 In the one embodiment of the present invention, the films hereof provide high opacity and low light transmission. A distinction should be made between opacity and light transmission.

10 Opacity is the opposite of transparency and is a function of the reflection of light which is incident on a film, and/or a function of the scattering of light transmitted through the film. Opacity is the ability of a film material to obscure what is under or behind the film. For example, the opacity of a film can be measured by its ability to block out writing which is  
15 below it.

Light transmission, on the other hand, is a function of the amount of light which a film will allow to pass directly through it. While opacity can be measured from the side of the film from which the light is incident, light transmission is measured  
20 from the opposite side of the film with respect to the incidence of the light. Light transmission and opacity are measured as disclosed in our EPA 0 536 917.

Accordingly, a highly reflective film may provide high opacity while allowing light transmission. This is because the  
25 percent of light transmission is not really related to the percent opacity. Light transmission is the amount of light passing directly through the film, and opacity is the amount of transmitted light which is prevented from passing back through the film. To prevent food spoilage, decreased light  
30 transmission is desirable, but opacity is of no particular concern.

Where the product of this invention is to be used as a label for goods, whether the label is opaque or transparent is a function of the objectives to be achieved. Where it is  
35 desired to hide the contents of the package being labeled, it would be preferable to use an opaque label. However, where it is more desirable to expose the contents of the package to

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customer examination, the label should be transparent. As noted in the beginning of this specification, where the package is opaque because the contents of the package are subject to spoilage by incident radiation, an opaque package and label is  
5 desirably used.

In forming the core layer, as in U. S. Patent No. 4,377,616, the disclosure of which is incorporated herein by reference in its entirety, a master batch technique can be employed by either: forming the void initiating particles in  
10 situ; or by adding preformed particles, usually spheres, to a molten thermoplastic matrix material. After the formation of a master batch, appropriate dilution of the system can be made by adding additional thermoplastic matrix material until the desired proportions are obtained. However, the components  
15 may also be directly mixed and extruded instead of utilizing a master batch method.

The void-initiating particles, which are added as filler to the polymer material of the core layer, can be any suitable organic or inorganic material which is substantially  
20 incompatible with the core material at the temperature of biaxial orientation. Where the core polymer material is a polyolefin, suitable incompatible filler materials are exemplified by polybutylene terephthalate, nylon, solid or hollow preformed glass spheres, metal beads or spheres, ceramic  
25 spheres, calcium carbonate, etc.

The polyolefin polymer contemplated as the core material according to this invention includes polypropylene, polyethylene, polybutene and copolymers and blends thereof. A particularly preferred core polymer material is an isotactic  
30 polypropylene containing at least about 80\*% by weight of isotactic polypropylene. It is also preferred that the polypropylene have a melt flow index of about 2 to 10 g/10 min.

It is preferred that the average diameter of the void-initiating particles be about 0.1 to about 10 microns. These  
35 particles may be of any desired shape, although it is preferred that they be substantially spherical in shape. This does not mean that every void or every void inducing particle are the

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same size. It means that, generally speaking, each void tends to be of substantially similar shape when similarly shaped and sized particles are used even though they vary in dimensions. These voids may assume a shape defined by two opposed end edge  
5 contacting concave disks.

Experience has shown that optimum characteristics of opacity and appearance are obtained when the two average major dimensions of substantially all of the voids are greater than about 30 microns. The void-initiating particle material, as  
10 indicated above, should be incompatible with the core material, at least at the temperature and under the conditions of biaxial orientation.

The core has been described above as being a thermoplastic polymer material, within which are located strata of voids.  
15 From this it is to be understood that the voids create the matrix configuration. The term "strata" is intended to convey the understanding that there are many voids creating the matrix and the voids themselves are oriented so that the two major dimensions are aligned in correspondence with the direction of  
20 orientation of the polymeric film structure. After each void has been formed through the initiation of the described particle, the particle generally contributes little else to the system. This is because the refractive index of the void initiating particle is not usually a controlled parameter. It  
25 can be very distinct from the refractive index of the core polymer, or it can be close enough to the core polymer material that it makes no contribution to opacity. When the latter is the case, the opacity is principally a function of the light scattering effect which occurs because of the existence of the  
30 voids in the system.

A typical void in the core matrix, which has been created by biaxial orientation of a suitable core polymer material containing void forming particles, is defined as having, after  
biaxial orientation, major dimensions X and Y, and a minor  
35 dimension Z. The dimension X is the dimension substantially parallel to the machine direction orientation of the composite film, and the dimension Y is the dimension which is

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substantially parallel to the transverse direction orientation of the composite film. The dimension Z approximately corresponds to the cross-sectional dimension of the void initiating particle, which for the purposes of this analysis can be considered to be spherical.

It is a necessary part of this aspect of the present invention that the nature of the core polymer and the conditions of biaxial orientation must be such that, after biaxial orientation, the X and Y dimensions of the voids in the core be significantly larger than the Z dimension. Thus, if the Z dimension generally approximates the cross-sectional dimension of the spherical particle initiating the void, and the biaxial orientation of the core matrix causes voids to form which will render the film opaque. Thus, the X and Y dimensions must be significantly greater than Z.

By way of illustration, room temperature biaxial orientation of a core matrix, comprising a polypropylene polymer admixed with polybutylene terephthalate (PBT) spheres of a size and amount contemplated herein as the void forming particles to thereby make up the core matrix, does not produce the instant desired structure. Under these conditions, with this polymer, room temperature orientation will cause the polymer area around the void initiating particles to either split, or, if any voids are created, they will be of a size which is too small to achieve the objects of this invention, which is to opacify the film. This is because polypropylene must be oriented at a temperature significantly higher than its glass transition temperature. The temperature conditions must permit a void to be created having X and Y dimensions which are significantly greater than the size of the void initiating particle, and are preferably at least several multiples of this Z dimension, without splitting the polymer film, at least to any significant degree. If this is accomplished, optimum physical characteristics, including low water vapor transmission rates and a high degree of light scattering are obtained without splitting or fibrillating the film.

As indicated above, the matrix polymer and the void

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initiating particle must be incompatible in the sense that they are two distinct phases which do not blend when the resultant film made therefrom is mixed or stretched. The void initiating particles, which are preferably spherical, form a dispersed phase throughout the lower melting polymer phase, which polymer will, ultimately, upon orientation, become filled with voids containing the spherical particles positioned somewhere in the voids.

As a result of the biaxial orientation of the film structure herein, in addition to opacifying the core layer of the structure, the orientation improves other physical properties of the composite layers, such as: flex-crack resistance, Elmendorff tear strength, elongation, tensile strength, impact strength and cold strength properties. The resulting film can have, in addition to a rich, high quality appearance and excellent opacifying characteristics, low water vapor transmission rate characteristics and low oxygen transmission rate characteristics. These improved physical properties make the film ideally suited for packaging food products, even those comprising liquids. The film also has attractive utility as a decorative wrap material.

It is believed that because the void-initiating particles preferably have or approach the geometry of a sphere, the voids which are created upon orientation are closed cells. This means  
25 that there is virtually no path open through the core matrix, from one side of the core the other, through which liquid or gas can pass. In the composite film of this invention, even if there were some small amount of transmission available through the core material, the two skin layers would effectively seal  
30 the composite against transmission therethrough.

The increased opacity and decreased light transmission of the composite film of this aspect of this invention is quite satisfactory, but these can be further improved by the addition to the core layer of opacifying agents, which themselves may be known. Where additional opacifying agents are incorporated in the core matrix composition of this invention, they should be used in a proportion of up to about 10%, preferably at least

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about 1%, by weight. Suitable conventional opacifying agents can be added to the melt mixture of the core polymer and the void initiating particles before extrusion thereof into a film. It is within the scope of this invention for the conventional  
5 opacifying agents to also contribute to the formation of opacifying voids in the core polymer film, but they need not do so.

Opacifying compounds are generally well known in this area. They may be exemplified by iron oxides, carbon black, aluminum,  
10 aluminum oxide, titanium dioxide, and talc. The additional opacifying compounds being referred to herein are not required to contribute to formation of voids according to the practice of this invention, nor should they take the place of the void initiating components.

15 The polymer materials which are contemplated as the material for use in forming skin layer (c) are suitably exemplified by polyolefins and include, among others: polyethylene, including high density polyethylene, linear low density polyethylene, medium density polyethylene,  
20 polypropylene, polybutene, and copolymers thereof. These copolymers are exemplified by and include block copolymers, for example of ethylene and propylene, random copolymers, for example of ethylene and propylene, and other ethylene homopolymers, copolymers, terpolymers, or blends thereof.

25 Where homopolymer are to be used, they may be formed by polymerizing the respective monomer. This can be accomplished in a conventional manner by bulk or solution polymerization, as those of ordinary skill in this art will plainly understand.

Despite the fact that the selection of the composition of  
30 the (c) layer is from amongst a wide variety of materials: depending on the physical properties sought to be achieved, the ink receptive skin layer (b) must be selected from ethylene polymers having a density of 0.926 to 0.965 g/cc, or ethylene-propylene-butene-1 terpolymers. Preferably the density of the  
35 ethylene polymer skin layer should be 0.926 to 0.945 g/cc.

The contemplated terpolymers which may be used for the skin layers (b) and/or (c) are preferably polymers of low

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stereoregularity. These terpolymers can have a melt flow rate, at 446°F, of about 2 to about 10 grams per 10 minutes, preferably about 4 to about 6 grams per 10 minutes. The crystalline melting point of these terpolymers can suitably be  
5 from less than about 250°F up to somewhat greater than about 371°F. These terpolymers will often predominate in propylene, and the ethylene and 1-butene monomers, where present, should be in mole ratios, with respect to each other, of about 0.3:1 to 1:1, respectively.

10 As was the case for the core layer, the skin layer (c) can comprise an isotactic polypropylene polymer containing at least about 80% by weight of isotactic polypropylene. In this use, it is preferred that the polypropylene have a melt flow index of about 2 to 10 g/10 minutes.

15 Skin layer (c) can also be fabricated from any of the heat sealable copolymers, blends of homopolymers, and blends of copolymer(s) and homopolymer(s) heretofore employed for this purpose. Illustrative of heat sealable copolymers which can be used in the present invention are ethylene-propylene copolymers  
20 containing about 1.5 to about 10, and preferably about 3 to about 5 weight percent ethylene. Ethylene-propylene-butene terpolymers containing about 1 to about 10, and preferably about 2 to about 6 weight percent ethylene, and about 80 to about 97, preferably about 88 to about 95, weight percent propylene.  
25 Heat sealable blends of homopolymer which can be utilized in providing layers (b) and/or (c) include about 1 to about 99 weight percent polypropylene homopolymer, e.g. one which is the same as, or different from, the polypropylene homopolymer constituting core layer (a) blended with about 99 to about 1  
30 weight percent of a linear low density polyethylene (LDPE). If layer (c) is heat-sealable, corona or flame treatment of layer (c) may not be required.

Where it is important that the skin layer (b) to have high gloss, it has been found to be desirable to use a medium density  
35 polyethylene for this skin layer. It has also been found that this medium density polyethylene surprisingly imparts excellent adhesion and retention of U V cured inks to the composite film.

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Thus, where inks cured with the aid of UV are to be applied to the surface of a skin layer, it is most preferred in the practice of this invention to use medium density polyethylene as at least the ink receptive skin layer (b). Of course, where  
5 ink adhesion is an object to be achieved with the composite film of this invention, only the surface of the skin layer on which the ink is to be adhered needs to comprise medium density polyethylene.

The opacity, whiteness and low light transmission of the  
10 film is further enhanced by the addition to at least the first skin layer (b) of titanium dioxide in amounts of about 1% by weight and up to about 12% by weight. The titanium dioxide may suitably be added to the melt mixture of the skin layer before extrusion thereof, in substantially the same manner as in making  
15 the core composite material. Preferably, the first skin layer (b) contains from about 2% by weight to 6% by weight of  $TiO_2$ . Additionally, this layer may also contain talc. The whiteness resulting from the inclusion of  $TiO_2$  provides an excellent surface for graphics. Furthermore, the whiteness imparted by  
20 the titanium dioxide, and the use of medium or high density polyethylene, as the skin layer, allows printing on the laminated or unlaminated structures of this invention without requiring white ink.

The processability and machinability of the film may be  
25 enhanced by the inclusion in the polymeric material used to form the skin layer (c) of a small percentage of finely subdivided inorganic material. Preferably, this inorganic material has a means particle size from 0.2 to 5.0 micron. Such inorganic material not only can impart antiblock characteristics to the  
30 multi-layer film structure of the present invention, but also can reduce the coefficient of friction of the resultant film.

Contemplated finely divided inorganic materials, referred to above include aluminium silicate, sodium-aluminium silicate and dehydrated kaolinite; they are exemplified by: syloid, a  
35 synthetic amorphous silica gel, having a composition of about 99.7%  $SiO_2$ ; diatomaceous earth having a composition of, for example, 92%  $SiO_2$ , 3.3%  $Al_2O_3$ , and 1.2%  $Fe_2O_3$  which has an



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average particle size of about 5.5 microns, which particles are porous and irregularly shaped; dehydrated kaolinite (Kaopolite SF) having a composition of 55% SiO<sub>2</sub>, 44% Al<sub>2</sub>O<sub>3</sub> and 0.14% Fe<sub>2</sub>O<sub>3</sub>, which has an average particle size of about 0.7 microns, and which particles are thin flat platelets; and synthetic, precipitated silicates, for example Sipernat 44, a material having a composition of 42% SiO<sub>2</sub>, 36% Al<sub>2</sub>O<sub>3</sub>, and 22% Na<sub>2</sub>O, which has an average particle size of about 3-4 microns, and in which the particles are porous and irregularly shaped.

10 The polyolefin blends used to coextrude the multi-layer high opacity film structures contemplated herein are suitably formed by employing commercially available intensive mixers, such as those of the Bolling or Banbury type. Mixers of this type are suitably employed in mixing a concentrate of the finely  
15 divided inorganic material and the selected polymer until there is a uniform dispersion of the inorganic material in the polymer.

If desired, the exposed surface of skin layers (b) and/or (c) can be treated in a known and conventional manner, e.g. by  
20 corona discharge or flame, to improve their receptivity to printing inks and/or suitability for such subsequent manufacturing operations as lamination. An exposed treated or untreated surface of layer (b) and/or (c) may have applied to it, coating compositions or substrates such as another polymer  
25 film or a laminate; a metal foil, such as aluminum foil; cellulosic webs, e.g. numerous varieties of paper, such as corrugated paperboard, craft paper, glassine, cartonboard, nonwoven tissue, e.g. spunbonded polyolefin fiber, melt-blown microfibers, etc. The application may employ a suitable  
30 adhesive, e.g. a hot melt adhesive, such as low density polyethylene, ethylene-methacrylate copolymer; a water-based adhesive such as polyvinylidene chloride latex, and the like.

Heat sealable blends of copolymer(s) and homopolymer(s) suitable for providing layer (c) include: a blend of about 5 to  
35 about 19 weight percent of polybutylene and about 95 to about 81 weight percent of a copolymer of propylene (80 to about 95 mole percent) and butylene (20 to about 5 mole percent); a blend

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of about 10 to about 90 weight percent of polybutylene and about 90 to about 10 weight percent of a copolymer of ethylene (2 to about 49 mole percent) and a higher olefin, preferably an  $\alpha$ -olefin having 4 or more carbon atoms (98 to about 51 mole percent); a blend of about 10 to about 90 weight percent polybutylene and about 90 to about 10 weight percent of a copolymer of ethylene (10 to about 97 mole percent) and propylene (90 to about 3 mole percent); and, a blend of about 90 to about 10 weight percent of polybutylene, and about 10 to about 90 weight percent of a copolymer of propylene (2 to about 79 mole percent) and butylene (98 to about 21 mole percent).

If skin layer (c) is not heat sealable, and that property is desired, then a heat sealable layer (d) may be applied to its surface. It is preferred not to apply any further coating on top of the ink receptive surface. The heat sealable layer (d) may be, for example, vinylidene chloride polymer or an acrylic polymer applied over the skin layer (c). In the alternative, the skin layer (c) may be an inherently easily heat sealable material as described herein which is coextruded with the core and the skinlayer (b). Vinylidene chloride polymer or acrylic polymer coatings are preferred materials which may be applied to the exposed exterior surface of the skin layer.

It is preferred that all layers of the multi-layer film structures of the present invention be coextruded. After formation, the film is biaxially oriented. For example, when employing medium density polyethylene for one of the skin layers, polypropylene for the polymer of the core matrix, and polybutylene terephthalate as the void initiating particles, a suitable machine direction orientation may be achieved by stretching the composite film about 4 to about 8 times, and a suitable transverse orientation may be achieved by stretching the film about 4 to about 10 times at a drawing temperature of about 100°C to 170°C to yield a biaxially oriented film. Opaque films according to this invention may be about 1 mil, but where transparency is an essential property, the film may be thinner or thicker, e. g., up to about 0.5 mil. Suitably the films may have thicknesses up to about 3.5 mils.

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In accord with another aspect of this invention, it is desirable to provide a composite plastic film which is suited to use as a label stock. Label stocks need to have the attributes of good ink retention and the ability to  
5 preferentially adhere to a pressure sensitive adhesive, as compared to the ability of that adhesive to adhere to a release layer. Often, it is also desirable for the exposed surface of a label stock to have high gloss.

A suitable peelable label stock is often put up as an  
10 assemblage of components. In one such assemblage, the components include: a base liner, a release layer disposed on the base liner, and a label stock, with a suitable pressure sensitive adhesive disposed thereon, releasably adhered to the release layer on the base liner. In instances where the  
15 adhesive is a pressure sensitive adhesive, a release layer is disposed on the base liner. In other cases the adhesive may be one activatable by other means, such as, heat, solvent, etc. Where the adhesive is not pressure sensitive, but is activatable by some other means, a release liner is not needed.

20 For use as a base or core layer for label stock purposes, the composite film form material of this invention is preferably opaque, preferably white opaque, in order to provide an excellent contrasting background for printed material applied to the exposed surface of the label stock. A material, which  
25 has the good characteristics of excellent tensile strength, low permeability to moisture and other liquids, is a polypropylene core material cavitated in the special manner described above so as to produce a pearlescent opaque appearance.

According to this aspect of this invention, the skin  
30 material coextruded onto at least the ink receptive surface of the core film is a medium or high density polyethylene. By this is meant that the density of the polyethylene can be anywhere from about 0.926 - 0.965, preferably 0.926 to 0.945, g/cc. Such a preferred, medium density polyethylene when formed into one  
35 of the skins of the label stock structure will have a 45° gloss of 50 or greater.

This gloss characteristic of the product of this invention

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is at least as good as or better than that of coated paper label stock which is commercially available. It is to be understood that both sides of the core material may have skins thereon which have been co-extruded, such as medium or high density polyethylene. It is also contemplated that one side may carry a medium or high density polyethylene layer, while the opposite surface may carry no skin layer or may have any one of a variety of other skin surfaces with other characteristics as aforesaid. The gloss of the ink receptive layer (b) should preferably be high.

For example, the opposite skin material (c) can be cavitated or non-cavitated polypropylene, a copolymer of ethylene and propylene, where the proportion of ethylene is about 2-8%, or a terpolymer of ethylene, propylene, butene-1, etc. The surface of this skin material can be anything which will aggressively receive and hold thereon a coating of a suitable adhesive, such as a pressure sensitive adhesive. The strength of the bond between this skin and the adhesive applied thereto must be sufficient to cause the adhesive to remain adhered to the skin layer when separation occurs between the adhesive and a release surface carrying the same, and sufficient to tightly adhere the label to the surface upon which it will be placed. The second skin layer (c) may include an inorganic material, such as for example calcium carbonate, to provide for improved label cutting. As aforesaid, it may also be suitably cavitated in order to improve its die-cutability.

In the art of labeling, the label which is to be applied to a surface or a product is normally carried by a release sheet or surface. A common example of this type of label structure familiar to most automobile owners is the registration sticker issued by the city or county which must be applied to a windshield. This type of structure comprises a release sheet, one side of which has a release surface, such as of a silicone material or the like. Carried on this surface is the label or decal which must be affixed to the windshield. A pressure sensitive adhesive is affixed to the label or decal and it is through this adhesive that the label or decal is releasably

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affixed to the release surface. Of course, the adhesive may first be applied to the label before mating it with the release liner. When the decal or label is separated from the release sheet the pressure sensitive adhesive must preferentially  
5 adheres to the label or decal rather than the release sheet. By this means the label or decal is affixed to the windshield.

As indicated above, instead of a pressure sensitive adhesive, activatable adhesives can be employed for certain labeling techniques. For instance, when a label is to be  
10 applied about the full circumference of a package or bottle, water or other solvent can activate an adhesive stripe or strip applied to one end of the label. The label is then fixed in place by a slight overlap of the other end of the label. It has also be discovered that die cutting of labels is materially  
15 enhanced by including inorganic particles, such as calcium carbonate in the label skin layer close to the adhesive and/or release layer. These particles may also cause some cavitation as a result.

The following specific examples are presented herein to  
20 illustrate particular embodiments of the present invention and hence are only illustrative of this invention and are not to be construed in a limiting sense. Unless indicated to be on some other basis, all parts and percentages are by weight.

Coefficient of friction values referred to herein have been  
25 determined according to the procedure of ASTM D 1894-78, modified as follows: the film to film area of contact was 2 inches X 1 inch, instead of 2 1/2 inches X 2 1/2 inches set forth in the ASTM procedure. The mass of the sled was 100 grams rather than 200 grams and the sled speed was 6 inches per  
30 minute, the same as ASTM D 1894-78. Thus, the modified test was run at a condition of 50 grams/in.<sup>2</sup> rather than 32 grams/in.<sup>2</sup>.

Haze and gloss values referred to herein were determined according to the procedures of ASTM D 1003-61 and D 2457-70, respectively.

35 EXAMPLE 1

The film of this example was produced for comparison with the films produced in accordance with the present invention.

- 20 -

A mixture of 92 percent, by weight, isotactic polypropylene (MP = 320°F, melt index = 3), containing 8 weight percent polybutylene terephthalate (PBT), (MP = 440°F) as the core layer void-initiating material, is melted in an extruder, having a  
5 screw with an L/D ratio of 20/1, to provide the core layer mixture. A second extruder, in association with the first extruder, is supplied with the same isotactic polypropylene as the first extruder (without PBT), this second extruder is used to provide the skin layer. A melt coextrusion is carried out  
10 while maintaining the cylinder of the extruder for the core polymer material at a temperature sufficient to melt the core polymer mixture, i.e. about 450°F to about 550°F or higher. The polypropylene mixture of the second extruder being used to form the skin layers is maintained at about the same temperature as  
15 the polypropylene being used in fabricating the core layer. The mixture of the second extruder is split into two streams to enable the formation of skin layers on each surface of the core layer. As will be appreciated by those of ordinary skill in the art, rather than splitting the output of the second extruder  
20 into two streams, a third extruder could be used to supply the second skin layer mixture. Such an arrangement would be desired when the material used to form the second skin layer is different from that of the first skin layer, or when the thickness of the second skin layer is different from that of the  
25 first skin layer, etc.

A three-layer film laminate was coextruded with a core thickness representing about 80 percent of the overall extruded thickness, with the thicknesses of the skin layers in the resultant film sheet representing about 20 percent of the film  
30 thickness. The film was subsequently oriented eight (MD) by about five and one-half (TD) times using a commercially available sequential biaxially orienting apparatus to provide a multi-layer film structure. The machine direction (MD) orientation is conducted at about 285°F. and the transverse  
35 direction (TD) orientation is conducted at about 300°F. The resultant multi-layer film exhibits a lustrous, white appearance

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and the following properties:

	Film thickness	1.30 mills
	Density	0.62 g/cc
	Gloss	82%
5	Light transmission	22%
	Coefficient of friction	0.80

#### EXAMPLE 2

The film of this example was also produced for comparison  
10 with the films produced in accordance with the present invention.

As in Example 1, a mixture of 92 percent, by weight, isotactic polypropylene (MP = 320°F., melt index = 3), and 8 weight percent PBT (MP = 440°F.), as the core layer void-  
15 initiating material, is melted in an extruder with a screw of L/D ratio of 20/1 to provide the core layer mixture. A second extruder, in association with the first extruder, is supplied with the same isotactic polypropylene as the first extruder, to which is added 4 percent TiO<sub>2</sub>. This extruder was used to  
20 provide the skin layer mixture. A melt coextrusion is carried out under the same conditions as used in Example 1. Again, the mixture of the second extruder is split into two streams to enable the formation of skin layers on each surface of the core layer.

25 A three-layer film laminate was coextruded with a core thickness, again representing about 80 percent of the overall extruded thickness, with the thickness of the skin layers collectively representing about 20 percent of the film thickness. The resultant film sheet was subsequently oriented  
30 eight (MD) by about five and one-half (TD) times using a commercially available sequential biaxially orienting apparatus to provide a multi-layer film structure. The machine direction (MD) orientation is conducted at about 285°F. and the transverse direction (TD) orientation is conducted at about 300°F. The  
35 resultant multi-layer film exhibits a pleasing appearance of higher whiteness than the film of Example 1. The properties of

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the film so produced are as follows:

	Film thickness	1.30 mills
	Density	0.62 g/cc
	Gloss	69%
5	Light transmission	21%
	coefficient of friction	0.46

### EXAMPLE 3

A concentrate containing 93% by weight of a 4.5 melt index isotactic polypropylene and 10% by weight of Sipernat 44, a precipitated sodium-aluminum silicate of the following analysis: 42% SiO<sub>2</sub>, 36% Al<sub>2</sub>O<sub>3</sub>, and 22% Na<sub>2</sub>O, having a mean particle size of 3.5 micron, which is available commercially from Degussa Chemical Company is intimately melt-mixed in a Bolling mixer until the inorganic components are uniformly dispersed in the molten polypropylene. The melt concentrate is fed into a pelletizing extruder line and formed into a solid-pellet concentrate. A second concentrate containing 90% by weight of a 4.5 melt index isotactic homopolymer of polypropylene and 10% by weight of Kaopolite 1152, a dehydrated kaolinite of the following analysis: 55% SiO<sub>2</sub>, 44% Al<sub>2</sub>O<sub>3</sub>, and 0.4% Fe<sub>2</sub>O<sub>3</sub>, having a mean particle size of 0.7 micron, is prepared in the same manner and was also pelletized. The two pelletized concentrates are then melt-blended with additional isotactic polypropylene of 4.5 melt index, and after uniform mixing, the blend is formed into solid pellets. The composition is now 99.5% polypropylene, 2400 ppm Sipernat 44 and 3000 ppm by weight Kaopolite 1152.

A mixture of 92 percent, by weight, isotactic polypropylene (MP = 320°F, melt index = 4.5), containing 8 weight percent PBT (MP = 440°F), as the core layer void-initiating material, is melted in an extruder with a screw, having an L/D ratio of 20/1, to provide the core layer mixture. A second extruder, in association with the first extruder, is supplied with the same isotactic polypropylene as the first extruder, to which is added 4 percent TiO<sub>2</sub>. This second extruder was used to provide the first skin layer mixture. A third extruder, in association with the first and second extruders, is supplied with the pellets



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produced as described above, having a composition of 99.5% polypropylene, 2400 ppm Sipernat 44 and 3000 ppm by weight Kaopolite 1152. The third extruder is used to provide the second skin layer mixture.

5 A three-layer film laminate was coextruded with a core thickness again representing about 80 percent of the overall extruded thickness, with the thicknesses of the first and second skin layers each representing about 10 percent of the film's overall thickness. The resultant film sheet was subsequently  
10 oriented eight (MD) time by about five and one-half (TD) times using a commercially available sequential biaxially orienting apparatus to provide a multi-layer film structure. As in the previous examples, the machine direction (MD) orientation is conducted at about 285°F. and the transverse direction (TD)  
15 orientation is conducted at about 300°F. The resultant multi-layer film has a first side of higher whiteness than that of the film of Example 1 and a second side having an appearance substantially the same as that of Example 1. The properties of the film so produced are as follows:

20	Film thickness	1.20 mills
	Density	0.62 g/cc
	Gloss	90%
	Light transmission	21%
	Coefficient of friction	0.30

25 The coefficient of friction of the finished film not only is desirably low but also is stable over a range of conditions which simulate typical converting operations, involving temperatures reaching as high as 80°C. for three seconds. The percent gloss is considered to be remarkably good considering  
30 the excellent coefficient of friction and anti-block characteristics of the structure. Moreover, no blocking of slit rolls occurred even after holding for three days at 60°C.

#### EXAMPLE 4

35 The composite film structure of Example 3 is corona discharge treated on both sides thereof in order to improve its wettability and adhesion by inks or other surface layers which

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may tend to have inferior wetting and adhesion in the absence of corona discharge treatment. The finished film has the following characteristics:

	Gloss	90%
5	Coefficient of friction	0.30

This film demonstrates that the coefficient of friction of the surface of the film from Example 3 is unaffected by corona discharge treatment. It is known that amide-modified polypropylene films significantly increase in coefficient of friction upon such treatment and must thereafter be conditioned to restore the coefficient of friction to useable levels. Again, no blocking of slit rolls occurred after holding for three days at 60°C.

#### 15 EXAMPLES 5 AND 6

This example shows that the ink adhesion of the surface of a film of this invention is substantially improved as a function of the choice of polymer selected for the skin layer on which the ink will be disposed. It should be understood that the ink adhesion on the surface of the film is unrelated to the composition of any layer of the film except the surface skin layer. For comparison purposes, in all of the following tests, the core layer was made of clear, that is non-opaque, polypropylene.

25 In these examples, the ink was applied to the surface of two composite films having the surface compositions set forth hereinafter by a UV letter press process:

EXAM	SKIN RESIN	SKIN DENSITY	SKIN TREATMENT	ADHESION
5	MDPE	0.935 g/cc	FLAME (610 tape)	EXCELLENT
30 6	HDPE	0.952 g/cc	CORONA (810 tape)	FAIR

#### EXAMPLES 7 AND 8

In the following examples, the ink was applied by a UV screen process.

35 EXAM	SKIN RESIN	SKIN DENSITY	SKIN TREATMENT	ADHESION
7	MDPE	0.935 g/cc	FLAME (610 tape)	GOOD
8	HDPE	0.952 g/cc	CORONA (810 tape)	POOR

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EXAMPLES 9-13

In the following examples, the ink was applied by a UV screen process.

					ADHESION (600 TAPE)
5	EXAM	SKIN RESIN	SKIN DENSITY	SKIN TREATMENT	
	9	HDPE	0.952 g/cc	FLAME	GOOD
	10	HDPE	0.952 g/cc	CORONA	GOOD
	11	MDPE	0.941 g/cc	FLAME	EXCELLENT
	12	MDPE	0.941 g/cc	CORONA	EXCELLENT
10	13	PP			FAIL

EXAMPLES 14 AND 15

In the following examples, the ink was applied by a water based flexo process:

15

EXAM	SKIN RESIN	SKIN DENSITY	SKIN TREATMENT	ADHESION
14	MDPE	0.941 g/cc	FLAME (610 tape)	EXCELLENT
15	HDPE	0.952 g/cc	CORONA (810 tape)	EXCELLENT

20

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CLAIMS

1. A biaxially oriented, thermoplastic, polymeric, multilayer film structure which comprises :
  - a) a polymeric core layer; and
  - 5 b) a first ink-receptive skin layer comprising an ethylene polymer having a density from 0.926 to 0.965 g cm<sup>-3</sup> adhering to a surface of the core layer (a).
2. A film according to claim 1 wherein a second skin layer (c)  
10 is adhered to the other surface of the core layer (a).
3. A film according to claim 1 or 2 wherein at least one of the skin layers comprises medium density polyethylene (MDPE).
- 15 4. A film according to any preceding claim wherein at least one of the core layer (a) and skin layer (c) comprises isotactic polypropylene.
5. A film according to any preceding claim which is opaque.  
20
6. A film according to any preceding claim wherein at least one of the skin layers includes titanium dioxide.
7. A film according to any preceding claim wherein at least  
25 one of the core layer (a) and skin layer (c) comprises an opaque matrix of (i) a thermoplastic polymeric material in which are dispersed (ii) void-initiating solid particles which are phase-distinct from the thermoplastic polymeric material of the matrix and about which are located opacifying voids.
- 30
8. A film according to any preceding claim wherein at least skin layer (a) comprises a thermoplastic polymeric material which is thick enough substantially to prevent the asperities of the core layer from being manifest.
- 35
9. A film according to any preceding claim wherein skin layer (c) comprises an antiblock.

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10. A film according to any preceding claim wherein skin layer (c) comprises a heat sealable material.

5 11. A film according to any preceding claim wherein at least skin layer (c) is treated to modify the surface properties thereof.

12. A film according to any preceding claim wherein skin layer  
10 (a) has ink indicia applied thereto.

13. Use of a film according to any preceding claim as label stock.

15 14. Use according to claim 13 wherein the label stock is releasably adhesively bonded to liner stock.

20

25

30

35

1 / 1

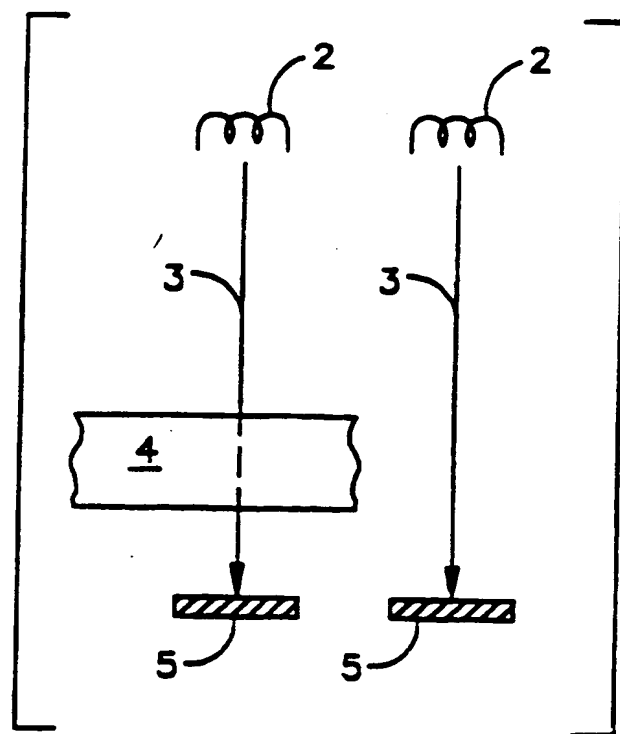


FIG. 1

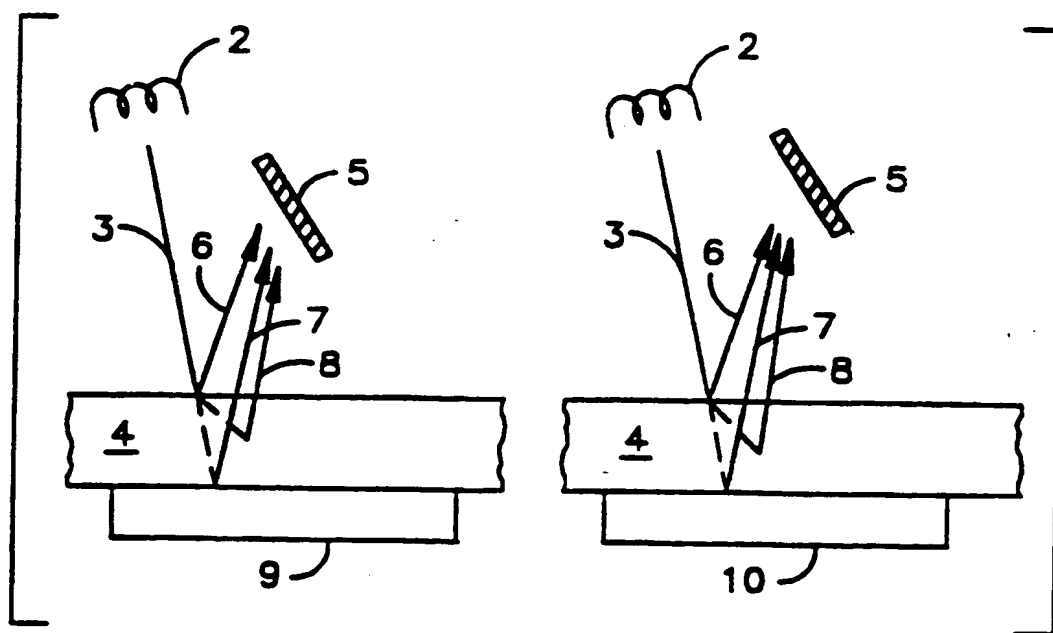


FIG. 2

SUBSTITUTE SHEET (RULE 26)

## INTERNATIONAL SEARCH REPORT

International application No.  
PCT/US93/12254**A. CLASSIFICATION OF SUBJECT MATTER**

IPC(5) : B32B 3/26, 27/08, 27/32

US CL : 428/314.4, 315.5, 315.9, 317.9, 319.7, 327, 516, 910

According to International Patent Classification (IPC) or to both national classification and IPC

**B. FIELDS SEARCHED**

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 428/314.4, 315.5, 315.9, 317.9, 319.7, 327, 516, 910

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

**C. DOCUMENTS CONSIDERED TO BE RELEVANT**

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US, A, 4,377,616 (ASHCRAFT) 22 MARCH 1983, see col. 1, line 42 to col. 2, line 20, col. 7, lines 25-41 and claim 1.	1-3
X, P	US, A, 5,176,954 (KELLER) 05 JANUARY 1993, see entire document.	1-3

☐ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

* Special categories of cited documents:	*T later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
*A* document defining the general state of the art which is not considered to be part of particular relevance	*X* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
*E* earlier document published on or after the international filing date	*Y* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
*L* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	*G* document member of the same patent family
*O* document referring to an oral disclosure, use, exhibition or other means	
*P* document published prior to the international filing date but later than the priority date claimed	

Date of the actual completion of the international search 10 FEBRUARY 1994	Date of mailing of the international search report 23 MAR 1994
Name and mailing address of the ISA/US Commissioner of Patents and Trademarks Box PCT Washington, D.C. 20231 Facsimile No. (703) 305-3230	Authorized officer CHRISTOPHER BROWN Telephone No. (703) 308-2351

Form PCT/ISA/210 (second sheet)(July 1992)\*

# INTERNATIONAL SEARCH REPORT

International application No.  
PCT/US93/12254

## Box I Observations where certain claims were found unsearchable (Continuation of item 1 of first sheet)

This international report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:  
because they relate to subject matter not required to be searched by this Authority, namely:
  
2. ☐ Claims Nos.:  
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:
  
3. ☒ Claims Nos.: 4-14  
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

## Box II Observations where unity of invention is lacking (Continuation of item 2 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

1. ☐ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.
2. ☐ As all searchable claims could be searched without effort justifying an additional fee, this Authority did not invite payment of any additional fee.
3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:
  
4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest

- ☐ The additional search fees were accompanied by the applicant's protest.  
☐ No protest accompanied the payment of additional search fees.